



Recent advances on mitigating wax problem using polymeric wax crystal modifier

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Abstract The petroleum industry has addressed wax problems since its inception. Every year, considerable resources are expended on wax removal, which accordingly cause significant economic loss. As one of the materials in chemical treatments, polymeric compounds referred to as “wax-crystal modifier”, is being widely used to improve flow properties and/or combat wax deposition for waxy crude oils. This article reviews the recent achievements with regard to the flow improvement and wax inhibition of waxy oils using traditional polymeric wax crystal modifiers, such as ethylene–vinyl acetate (EVA), poly(ethylene–butene) (PEB), and polyethylene–poly(ethylene–propylene) (PE-PEP), as well as the development of novel polymers for potential use in the near future. The goal of this review is to assist people understand the advances in this topic.

Keywords Waxy oil · Polymeric wax crystal modifier · Wax inhibition · Flow improvement · Recent advances

Introduction

It is well known that crude oil is a complex mixture containing paraffins, aromatic hydrocarbons, resins, and asphaltenes. Among them, paraffins are considered as a major challenge, especially for the upstream petroleum industry. The solubility of high-molecular paraffins is strongly related to the temperature. With the decreasing

temperature, these paraffins tend to precipitate and form stable wax crystals. The wax crystals will deposit on the pipe wall and/or transport with fluids, which would reduce the flowability of crude oils and plug pipelines or seize equipments, leading to costly downtime and expensive remediation techniques (Bacon et al. 2010; Bello et al. 2006).

Wax deposition occurs when the oil temperature is lower than the wax appearance temperature (WAT) and a temperature gradient exists between the crude oil and colder deposition surface (Jennings and Breitigam 2010; Venkatesan et al. 2012). This process usually includes three stages: (1) paraffin begins to crystallize forming a crystal nucleus when the temperature is below WAT; (2) paraffin crystals become larger with more paraffin molecules precipitating and growing upon the nucleus; (3) the grown crystals deposit on the surface of pipelines and production facilities (Zhang et al. 2014). Wax deposit gives rise to problems during crude production, storage, transportation, handling, and processing, which could cost up to billions of dollars a year worldwide (Towler et al. 2007).

Wax deposition: removal and prevention

Numerous methods have been established to handle wax deposition problem, which can be generally divided into two categories: removal and prevention. The removal techniques applied in oilfields include mechanical (pigging), thermal (hot water or oil), and chemical (solvents) methods; while, for the prevention or inhibition of wax deposition, dispersants and crystal modifiers are usually employed, and these chemicals are known as “wax inhibitor” (Dobbs 1999). In reality, a combination of two or more methods is usually used. Currently, the mechanical

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Fig. 1 Schematic representation of wax crystal modifier co-crystallization with wax crystals (source: Al-Yaari 2011)

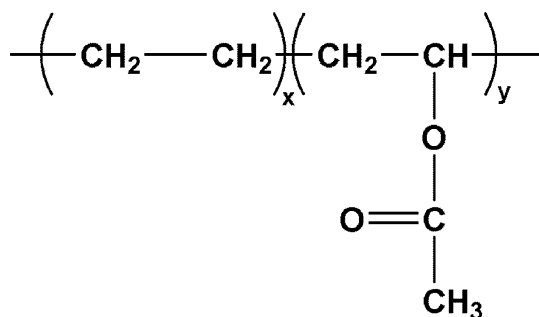
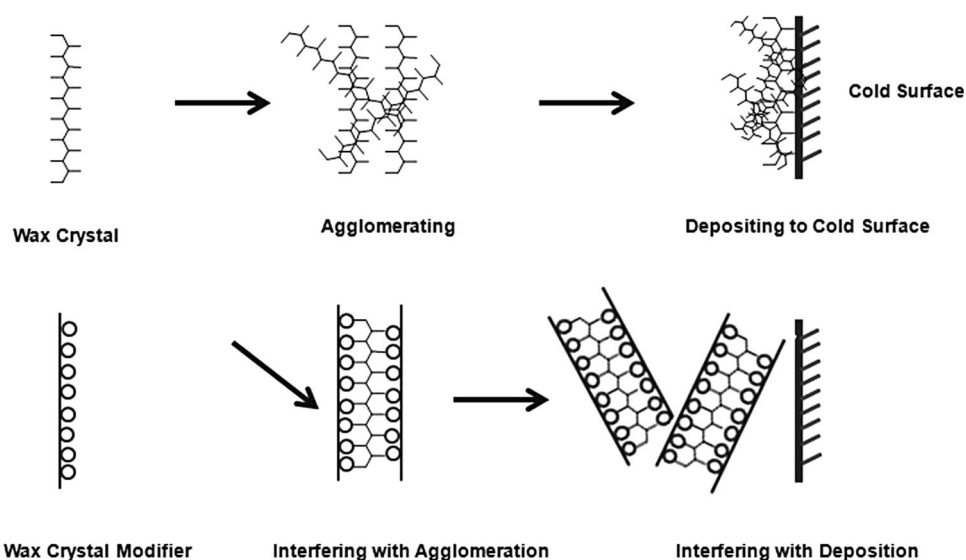


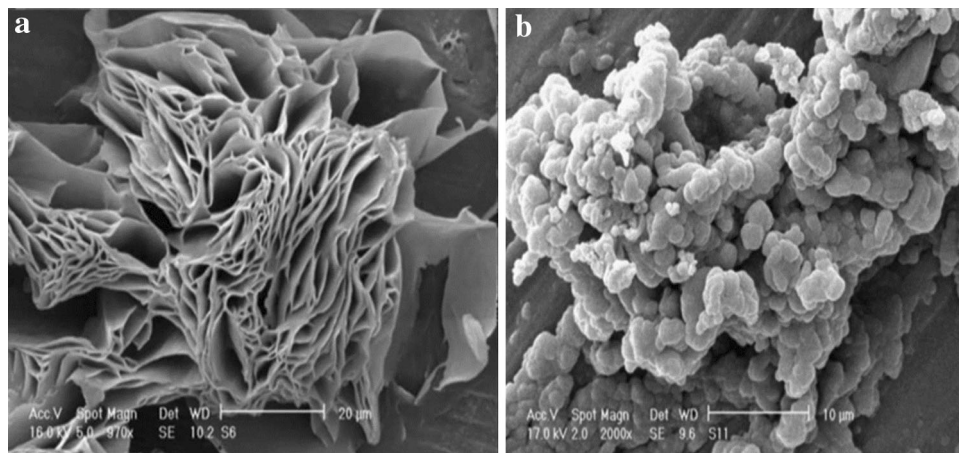
Fig. 2 Chemical structure of ethylene–vinyl acetate copolymer

method, pigging, is the most common wax removal technique, especially in the offshore subsea systems. However, this operation is suggested to be performed as seldom as possible due to the high cost. The actual cost of operating pigging may be not very significant, but the potential cost associated with using pigging such as deferred production is substantial. Therefore, in the interest of having more

economic return, pigging frequency must be markedly reduced. This is the main reason that wax crystal modifiers are being so extensively used. Although this kind of chemicals cannot provide complete wax inhibition, they can effectively reduce the wax deposition rate and in turn delay the build-up of wax deposits (Pedersen and Rønningsen 2003).

Wax crystal modifiers are materials that have similar chemical structure to the wax that is precipitating. The typical wax crystal modifiers are polymeric compounds constituted by one or more hydrocarbon chain(s) (wax-like) and polar portion. This type of compounds can co-precipitate or co-crystallize with wax by occupying the position of wax molecules on the crystal lattice through the hydrocarbon chains; meanwhile, it also places a steric hindrance on the crystal which can interfere the growth and aggregation of wax crystals, and frequently reduce the pour point of crude oils (Machado et al. 2001; Paso and Fogler 2004). This process is clearly illustrated in Fig. 1 (Al-Yaari 2011).

Fig. 3 SEM images of wax crystals without EVA (a) and with 100 ppm EVA (b) (source: Jafari Ansaroudi et al. 2013)



In this paper, recent works related to flowability improvement and/or wax inhibition of waxy oils using conventional and novel polymeric wax crystal modifiers are reviewed, aiming to provide an up to date synopsis of this issue.

Ethylene–vinyl acetate (EVA)

Compared to other polymers, ethylene–vinyl acetate copolymers (EVA) are the most extensively used wax crystal modifiers. This kind of copolymers has a linear chain composed of polyethylene portion with varying length depending on the quantity of co-polymerized monomer (vinyl acetate). The chemical structure of EVA is shown in Fig. 2. It has been recognized that the EVA copolymers exhibit varying degree of capacity in controlling the size of formed wax crystals (Vieira et al. 2012). When EVA is successfully used, the produced crystals are considerably smaller and more numerous than those crystallized from untreated systems (Petinelli 1979).

The influence of EVA copolymers containing different content of vinyl acetate on the viscosity and pour point of a Brazilian crude oil was investigated by Machado et al. (2001). The results revealed that EVA 30 (vinyl acetate content: 30 wt%) is the most efficient copolymer for pour point depression compared to other evaluated copolymers which have 20, 40, and 80 wt% of vinyl acetate. A similar tendency was also observed by Petinelli (1979) and Yang et al. (2009). In addition to the content of vinyl acetate, it seems that the molecular weight and polydispersity of EVA copolymers also affect the phase behavior and pour point depression of crude oils. Jiang et al. (2006) found that the optimum molecular mass of EVA for pour point depression is 1.2×10^4 Da, but the influence of the relative molecular mass distribution is negligible. This conclusion might be appropriate for asphaltene-free oils; however, for the asphaltene oils, the situations would become more complicated (Taraneh et al. 2008).

The effect of asphaltene on the EVA performance with respect to flow properties' enhancement of wax synthetic systems (a solvent mixture, paraffin, and petroleum asphalt residue) was given by Brar and Kumar (2002). This study proved that the presence of petroleum asphalt residue would reduce the efficiency of the EVA copolymers. Consistent with previous reports, the vinyl acetate content of 32 wt% is the optimum composition for most of the

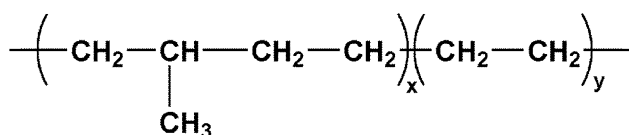


Fig. 4 Chemical structure of polyethylene–poly(ethylene–propylene)

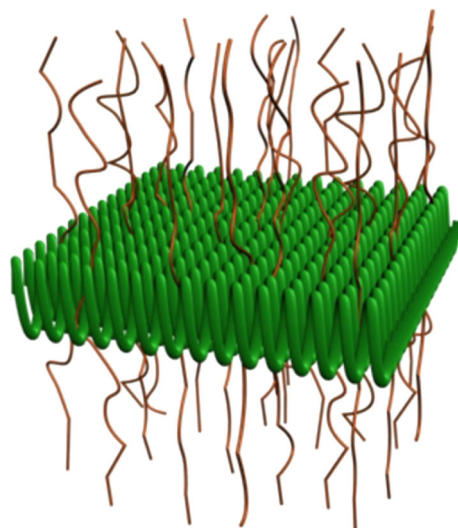


Fig. 5 Self-assembly of polyethylene–poly(ethylene–propylene)

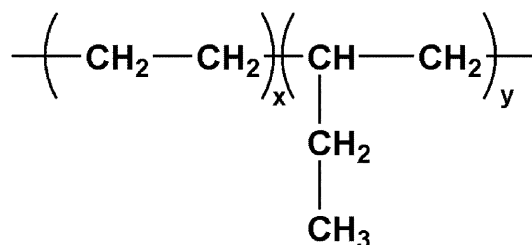


Fig. 6 Chemical structure of poly(ethylene–butene)

cases. Moreover, this copolymer (EVA 32) was found to be more efficient for the systems composed of high carbon number paraffins. This pioneer work was followed by Ashbaugh et al. (2005) who suggested that at the same dosage of EVA, the efficiency of flowability improvement decreases with the decreasing wax carbon number, which is somehow consistent with Brar and Kumar's findings. They also stated that the EVA copolymers could remarkably reduce the size of wax crystals, as well as change the particle from plate-like to a more compact and spherical morphology. Very similar phenomenon was obtained by Jafari Ansaroudi et al. (2013) who used scanning electron microscopy (SEM) to observe the morphology of wax crystal as shown in Fig. 3.

Marie et al. (2005) described the crystallization process of paraffins from solution in the presence of EVA copolymers (28 wt% vinyl acetate; $M_w = 10,800$ g/mol). The experimental data indicated that the mechanisms of crystal formation and growth are different depending on the type of solvent and distribution of paraffin molecule length. EVA can function either as a nucleating agent or a growth inhibitor. Due to close energies of interaction between different paraffin-like components, minor changes of experimental conditions may lead to dramatic effects.

In terms of solvents, it is well known that wax inhibitors are usually formulated with active compounds (crystal modifiers) dissolved in organic (aromatic) solvents for oilfield use (Jennings and Newberry 2008). In other words, the performance of the wax crystal modifiers may be further improved if a synergistic effect exists between EVA and solvent(s). Lashkarbolooki et al. (2011) evaluated several solvents and eventually proposed an optimum formulation for wax inhibition, i.e., 50 wt% EVA + 25 wt% Acetone + 25 wt% *p*-xylene, which could give up to 53 % reduction in the amount of wax deposition. Therefore, the formulation of wax inhibitors must be optimized before application due to the significant influence of solvent(s) (Qian et al. 2002).

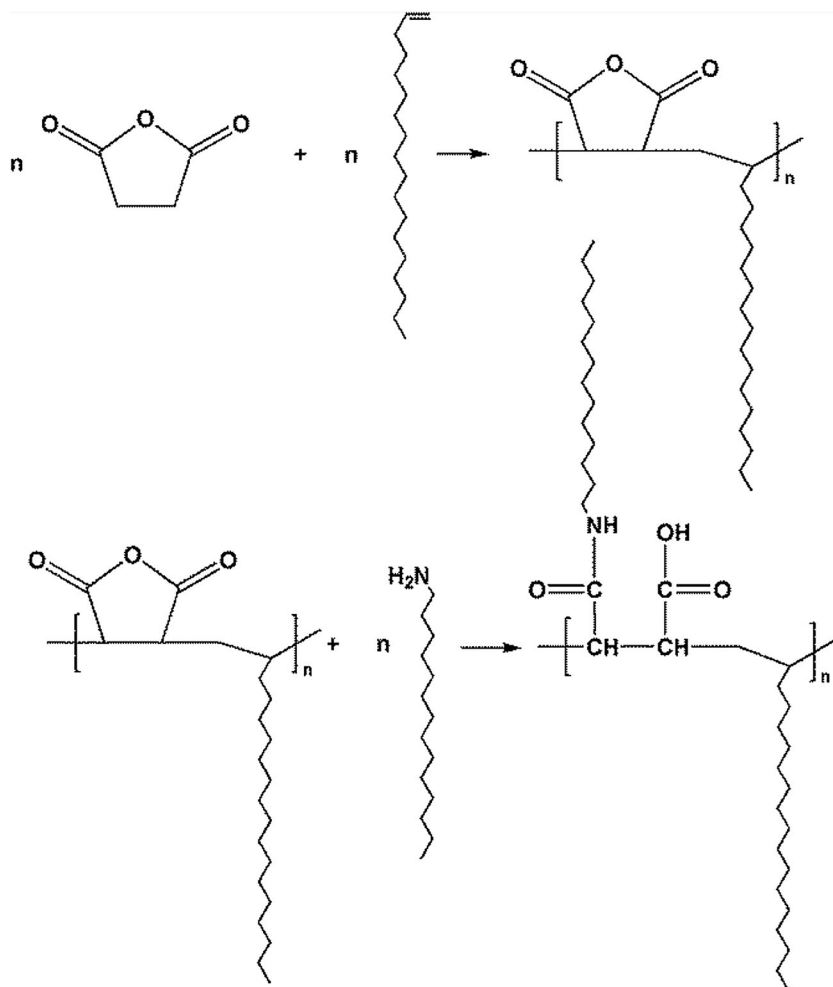
Theoretical studies of wax inhibition using EVA copolymers were performed by Lindeman and Allenson (2005) and Zhang et al. (2008). Lindeman and Allenson provided a new approach using theoretical modeling to correlate the molecular structure of polymer with the experimental physical properties, which can be used to predict the wax inhibition performance of EVA copolymers. While, Zhang et al. established a simple rational

model to estimate the minimum dosage of EVA-type copolymers for oils with different paraffin contents. The other interesting research was conducted by Wu et al. (2005) who successfully used molecular dynamic simulation to explore the interaction mechanism between crystal planes of wax and EVA, as well as its derivatives with branches of propylene and butylenes, respectively. This simulation indicated that EVAP with one branch (propylene) adjacent to the VA group is a better flow improver than EVA.

Polyethylene-poly(ethylene-propylene) (PE-PEP)

Polyethylene-poly(ethylene-propylene) diblock copolymers have been demonstrated to be able to function as nucleators for wax crystal size control in middle distillate fuels (Leube et al. 2000; Monkenbusch et al. 2000). Figure 4 shows the chemical structure of PE-PEP. This type of copolymers undergoes self-assembly to yield plate structure, which in turn serves as wax crystal nucleation platform promoting nucleation of long-chain paraffins through

Fig. 7 Synthesis of poly(maleic anhydride amide co- α -olefin)



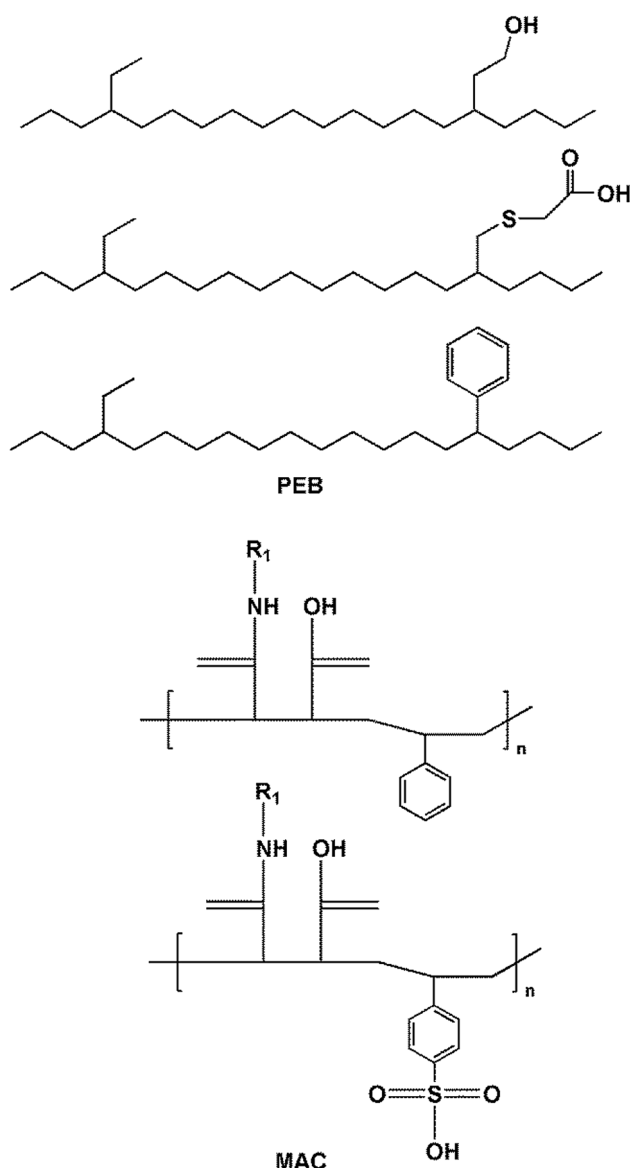


Fig. 8 PEB and MAC polymers with polar and/or aromatic modifications ($R = 12, 22$)

Table 1 Physical properties of waxy oil and the corresponding measure techniques

Properties	Techniques
Wax deposition	Coldfinger, Cold disk, Cold spot test, etc.
Wax morphology	Scanning electron microscopy(SEM), optical light microscopy, cross-polarized microscopy (CPM)
Formation of wax	X-ray diffraction
WAT or cloud point	CPM, differential scanning calorimetry (DSC), visual observation (ASTM method), viscometry
Pour point	Visual observation (ASTM method)
Flowability	Viscometry, yield stress, flow loop test

providing large PE surface area. Afterwards, expansive aggregates are formed consisting of a PE core cloaked behind the amorphous PEP brush layer as illustrated in Fig. 5. This characteristic makes PE-PEP copolymers promising flow improvers for waxy crude oils (Ashbaugh et al. 2002; Schwahn et al. 2002b). However, researches addressing the application and mechanism of PE-PEP in flow improvement and/or wax inhibition are rarely reported in recent years.

Poly(ethylene–butene) (PEB)

The interesting behaviors of PE-PEP aroused researchers to evaluate other polymer architectures, in which semi-crystalline and amorphous are combined in an alternating pattern as presented in Fig. 6. As one of such candidates, poly(ethylene–butene) (PEB) has attracted significant research attentions.

Schwahn et al. (2002a) studied the co-crystallization process of a PEB random copolymer with C_{24} . It was observed that, contrary to PE-PEP, the random PEB co-crystallizes with wax in thin sheets constituted of a single paraffin layer surrounding by amorphous polymer hairs on both plate sides. Meanwhile, polymer is homogeneously distributed in the wax-stabilized plate indicated by the well-defined polymer brush.

Intensive investigations of the interaction between wax and PEB polymers were conducted by Guo et al. (2004b). According to their experiments, the addition of PEB polymers to long-chain wax solutions in decane leads to heterogeneous nucleation on cooling. Wax tends to crystallize into quite complex shape such as rod-like or shuttle-like structures under the interference of PEB. These structures can reduce the yield stress of waxy oils compared to the plate-like crystals formed in the absence of PEB (Guo et al. 2004c, 2006; Tinsley et al. 2007a). In addition, they provided a kind of hydroxyl-grafted PEB polymer (PEB-OH), which seems more efficient in reducing the yield stress of asphaltene-contained crude oils than PEB which can be interpreted by the dispersion effect of the polar group ($-OH$) (Guo et al. 2004a).

Radulescu et al. (2006 and 2004) evaluated the performance of PEB 7.5 (7.5 ethyl branches per 100 backbone carbons) on co-crystallizing different paraffin waxes (C_{24} and C_{36}) from solutions. This evaluation revealed that the efficiency of PEB 7.5 in controlling the crystallization of long wax molecule (C_{36}) is relatively greater than that of short wax molecule (C_{24}). However, for a certain wax molecule, Guo et al. (2004c) claimed that PEB 10 which has an average 10 ethyl branches per 100 backbone carbon is more active in reducing the yield stress than PEB 7.5.

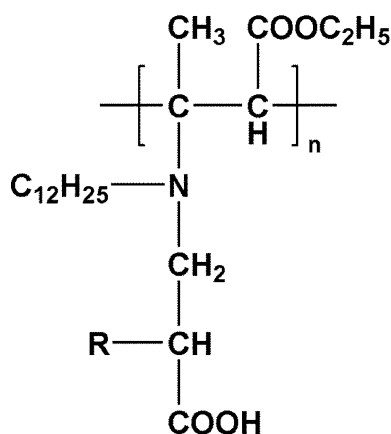


Fig. 9 Chemical structure of the hydrophobically modified polybetaines

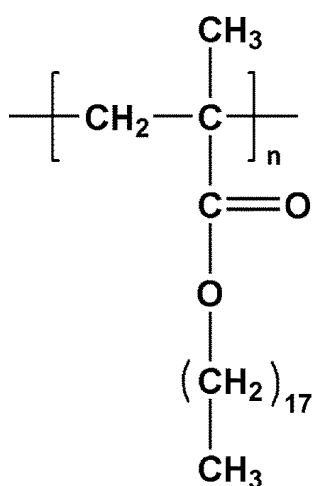


Fig. 10 Chemical structure of ODMA

These experimental results suggest that the overall performance of wax crystal modifiers is dependant not only on the wax structure but also on the structure of themselves (Ashbaugh et al. 2005).

In a more recent work, Radulescu et al. (2011) investigated the self-assembling behavior of multiblock copolymer consisting of PEB-*n* random polymers, in which the association mechanism was proposed aided by the investigation of these multiblock polymers in the presence of waxes.

Poly(maleic anhydride amide co- α -olefin) (MAC)

Poly(maleic anhydride amide co- α -olefin) (MAC) is another class of polymeric additives for waxy crude oils, which has been commercially used to retard wax deposition. Figure 7 shows the synthesis route of poly(maleic anhydride amide co- α -olefin) (Xu et al. 2009; Li et al. 2012).

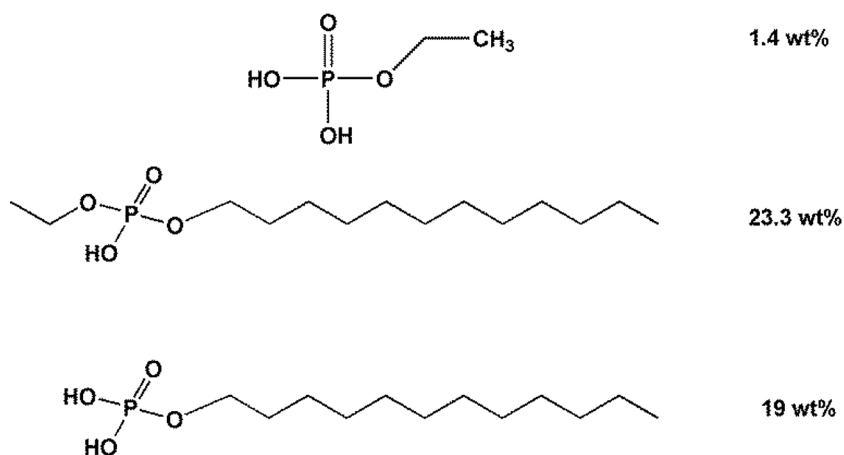
Del Carmen García (2000) investigated the effect of heavy linear alkanes (C24+) concentration on the effectiveness of MAC polymers on wax inhibition. It was demonstrated that C24+ waxes are deleterious for the efficiency of MAC functioning as a wax crystal modifier. Moreover, the presence of flocculated asphaltenes in crude oil would generate crystallization sites, which increase the cloud point of the crude oil and interfere with the crystal inhibition of MAC.

Tinsley et al. (2007a, b) compared the performance of three effective polymeric wax crystal modifiers, EVA, PEB, and MAC, using a laboratory deposition cell. In terms of the efficiency in yield stress reduction, these polymers could be ranked as PEB, EVA followed by MAC. While, the effects of altering microcrystallinity or alkyl appendages had minor affects compared to polymer type. It was also found that MAC polymers produced the largest alteration in crystal structure. A further investigation performed by Tinsley et al. (2009) was to examine the effects of a set of polymer additives (PEB and MAC) having controlled crystalline and polar content (Fig. 8) on asphaltene waxy oil. Results indicated that the presence of polar functionalities designed to target interaction with asphaltene was not beneficial. MAC polymers seem behave better than PEB polymers. Furthermore, the efficiency of yield stress reduction increases with the length of wax molecule, which can be attributed to the ability of polymers to co-precipitate with wax. Asphaltene has different effects on polymer performance depending on the property being measured. Table 1 lists physical properties of waxy oil and the corresponding measure techniques that have been applied.

Xu et al. (2009) presented a work entitled how comb-type poly(maleic acid alkylamide-co- α -olefin) assembles in waxy oils and improves flow ability, in which the performance of a series of MACs with different side-chain lengths was evaluated. It was proved that MAC polymers either self-assemble to nucleate the crystallization of paraffins or co-crystallize with them to inhibit wax crystal growth. The polarized-light microscopy observations demonstrated that the size of wax crystals was reduced significantly by MAC polymers. MAC 18-18, which has the longest side chains, is more efficient in improving the flowability of crude oils relative to MAC 12-18 and MAC 12-12.

Li et al. (2011) studied the crystallization of long-chain paraffins from solutions by X-ray diffraction. Upon addition of PEB or MAC, the low-angle scatterings from the layer structures were reduced and even disappeared. This fact implies that these polymers anchor into crystals by co-crystallization with paraffins and the non-crystallizable portion of the polymers provided a steric barrier against platelet stacking. For waxy crude oils containing

Fig. 11 Chemical structures and contents of the commercial phosphoric ester mixture



asphaltene, MAC was proved to be more effective than PEB in improving the flowability. The interaction between the carboxyl and amide groups of MAC with the polar aromatic asphaltenes appears to stabilize crudes through the steric effect of the long alkyl groups (Guo et al. 2005; Li et al. 2012).

Newly developed polymers

EVA, PE-PEP, PEB, and MAC could be classified as the conventional wax crystal modifiers. Based on the above extensive investigations, some novel polymeric compounds have been successfully synthesized in the past few years.

Didukh et al. (2004) synthesized a new type of hydrophobically modified polybetaines (Fig. 9), which could be employed as flow improver for waxy oil. When this polymer dissolved in *n*-heptanes, the pour point of crude oil was decreased by 18 °C. While, for yield stress reduction, the best formulation was obtained when it was dissolved in *o*-xylene, approximately seven times yield stress could be reduced in comparison with crude oil itself. The performance of this polymer for a Malaysian waxy crude was systematically evaluated by Halim et al. (2011). As a conclusion, 1,000 ppm is the optimum dosage.

A synthetic polymer, polyoctadecylmethacrylate (ODMA), was used for wax inhibition by Wang et al. (2003). The chemical structure of ODMA is presented in Fig. 10. In this study, the ability of ODMA compared to some commercial wax inhibitors with respect to WAT depression and wax deposition was evaluated. In the case of ODMA, the wax deposition was decreased by more than 50 %. However, it has no discernible effect on heavy paraffin (C₃₅ and above) deposition, which is similar for most of the commercial chemicals.

Gentili et al. (2005) synthesized three polymeric additives through the reaction of a commercial phosphoric ester mixture and sodium aluminate. The structure and content

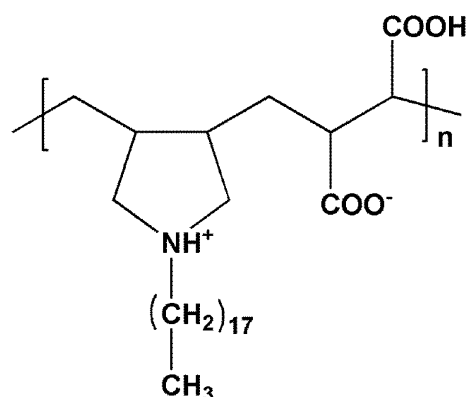


Fig. 12 Chemical structure of poly[*N,N*-diallyl-*N*-octadecylamine-*alt*-(maleic acid)]

of the commercial phosphoric ester mixture are shown in Fig. 11. The molecular weight of the product was controlled by the content of the reagent. It was demonstrated that the waxy oil was maintained at a low viscosity after treated with them. Regarding crystallization process, it seems that this type of polymers does not alter the manner of paraffin crystallization, but avoid the agglomeration of the wax crystals.

A hydrophobically modified polymer, namely poly(*N,N*-diallyl-*N*-octadecylamine-*alt*-(maleic acid)) (Fig. 12), was synthesized by Kudaibergenov et al. (2005). This polymer was exhibited to act as an efficient flow improver and wax inhibitor for a waxy crude oil (Askshabulak Oilfield). The efficiency of the polymer results from the presence of long hydrophobic chains and strongly interacting zwitterionic moieties.

A group of maleic anhydride-based copolymers was developed by Soni et al. (2005, 2008, 2010). Some of examples are given in Fig. 13. They found that all the synthetic polymers satisfied most of the requirements for flowability improvement and wax inhibition of waxy oils. In the case of polymer b and c, the percentage of wax

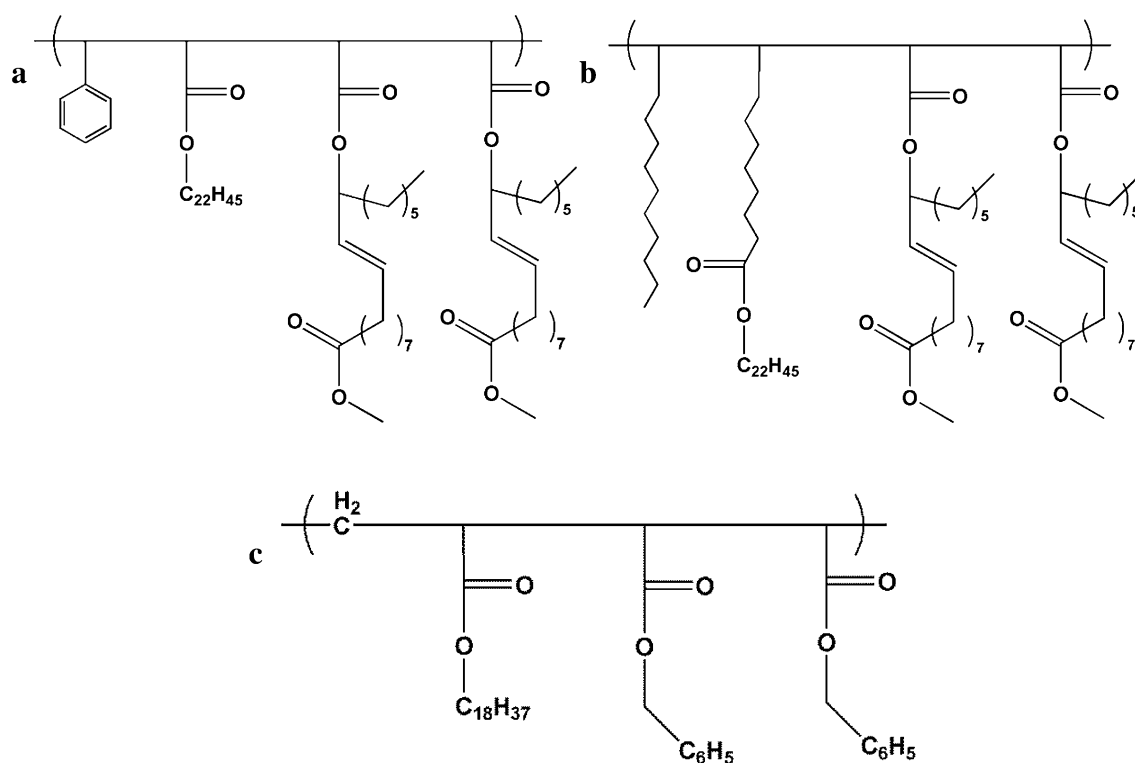


Fig. 13 Chemical structures of maleic anhydride-based copolymers

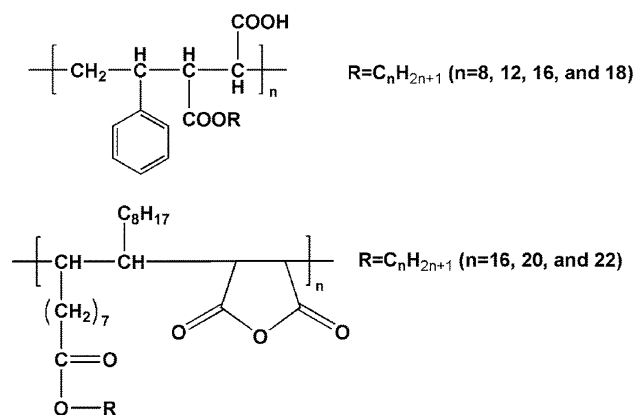


Fig. 14 Chemical structures of styrene maleic anhydride copolymer (upper) and poly alkyl oleate-co-succinic anhydride (bottom)

inhibition was up to 63 and 67 %, respectively. These excellent performances could be attributed to the presence of hydrocarbon chains, double bonds, and/or aromatic parts. Similarly, structural polymers were synthesized by

Al-Sabagh et al. (2009, 2013) as shown in Fig. 14. The experimental data indicated that all the polymers imposed a positive effect on the viscosity corresponding to improved flowability. Nevertheless, the maximum efficiency was obtained from the samples which have the longest branch chains (C18, left; C22, right), which is in agreement with the report elsewhere (Xu et al. 2009).

El-Ghazawy and Farag (2010) investigated the performance of docosanyl acrylate-co-(octadecyl or hexadecyl acrylate)-co-maleic anhydride terpolymers as flow improvers. In this study, the influence of composition and concentration of terpolymers on yield stress reduction of two crudes were examined and the optimum conditions were proposed.

A series of novel polymeric crystal modifiers, polyaminoamide (PAA), were prepared by aminolysis and polycondensating using vegetable oil as shown in Fig. 15 (Chen et al. 2011). Through evaluations, it was proved that all the PAA polymers are effective in inhibiting wax deposition, in which PPC-2 derived from canola oil and polyethylene

Fig. 15 Synthesis route of polyaminoamide (PAA)

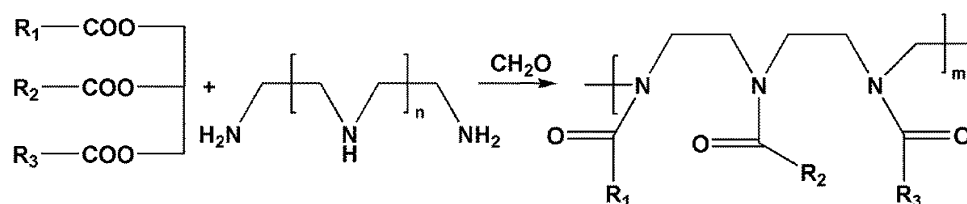


Fig. 16 Polarizing light micrographs of crystal in crude (left) and in PPC-2 treated crude (right) (source: Chen et al. 2011)

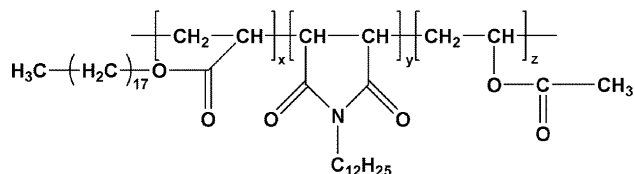
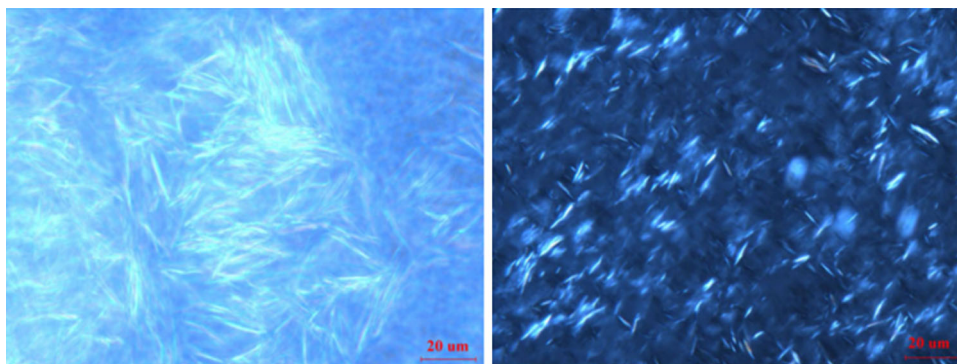


Fig. 17 Molecular formula of MAVA

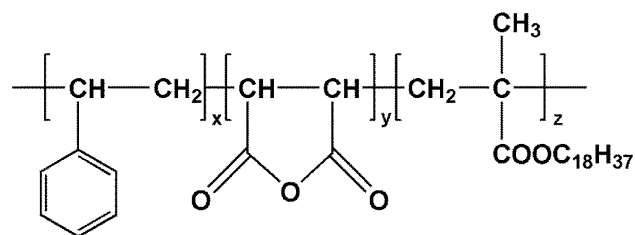


Fig. 18 Chemical structure of the terpolymer OMS

polyamine shows the highest inhibition efficiency of 66.2 %. After treated with PPC-2, the size of wax crystal in simulated crude was significantly reduced as shown in Fig. 16.

A new aminated copolymer (MAVA) functioning as a pour point depressant was synthesized by amination of terpolymer copolymerized with monomers octadecyl acrylate, maleic anhydride, and vinyl acetate (Fig. 17) (Fang et al. 2012; Zhang et al. 2009). After treated with the mixture of MAVA and EVA (mass ratio = 1:3) at the dosage of 400 ppm, the pour point of Shengli crude was dropped by 11 °C. It was also found that the presence of asphaltene, resin, and pour point depressant plays a positive role in flowability enhancement through formation of nucleators of the wax crystals.

Another terpolymer (Fig. 18) was synthesized by Shang et al. (2013) using octadecyl methacrylate (O), maleic anhydride (M) and styrene (S) as monomers of polymerization. This reaction was initiated by benzoyl peroxide (BPO). This polymer can depress the wax deposition rate of the Xinjiang oilfield crude by 50 %. Moreover, the pour point and viscosity were also reduced after the crude treated with it.

Zhang et al. (2010, 2011, 2012) discussed some factors leading to serious wax deposition, such as wax carbon

number, asphaltene and resin content, and gas–oil ratio, after which the performance of a polymeric wax crystal modifier consisted of polar and non-polar groups combining with surfactant was evaluated using five crudes. The results show that this mixture exhibits good wax inhibition functionality. The inhibiting rate can reach up to 66 %.

Conclusions

The primary objective of this paper is to review the recent advances on polymeric compounds that have been used as wax crystal modifiers for flowability improvement and/or wax inhibition in the petroleum industry aiming to provide an up to date overview of this topic. Based on the discussion, the following conclusions can be made:

1. The performance of wax crystal modifiers is strongly dependant on the capacity of polymer to co-crystallize with wax; in other words, it is related not only to structure of polymers but also to the composition of wax. For example, EVA 30 which contains 30 wt% of vinyl acetate is the most efficient polymer than EVA 20, 40, and 80; meanwhile, this copolymer is more effective for the systems having high carbon number paraffins. The efficiency of MAC polymers as flow improvers increases with the length of side chains.
2. Wax crystal modifiers are usually used combining with solvents, through which the wax inhibition efficiency could be further improved.
3. Asphaltenes exhibit different effects on the performance of wax crystal modifiers depending on the measured properties, such as yield stress, pour point, and wax deposition.
4. Numerous polymeric wax crystal modifiers have been experimentally investigated. However, theoretical modelings are extremely necessary to correlate the molecular structure of polymers with the corresponding performance to predict the efficiency of wax inhibition.

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